(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 450 777 B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
05.06.1996 Bulletin 1996/23

(51) Int Cl.[6]: **C08L 67/04**
// (C08L67/04, 101:00)

(21) Application number: **91302168.9**

(22) Date of filing: **14.03.1991**

(54) **Biodegradable plastics composition**

Biologisch abbaubare Kunststoffzusammensetzung

Composition de matière plastique biodégradable

(84) Designated Contracting States:
DE IT

(30) Priority: **06.04.1990 JP 92816/90**
06.04.1990 JP 92817/90

(43) Date of publication of application:
09.10.1991 Bulletin 1991/41

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Description

This invention relates to a biodegradable plastics composition. More particularly, this invention relates to a biodegradable plastics composition containing polyglycolide and one or more specific high molecular weight substances.

Plastics are widely utilized in daily life in the form of shaped articles such as films, bags and containers. As the majority of plastics are not decomposed in the natural environment, however, a serious problem of environmental pollution due to waste plastics has arisen. Accordingly, moves to prohibit or limit the use of plastics as packaging materials have been encouraged in recent years in Europe and America. Another approach to the problem is the development of plastics which are decomposable (biodegradable) by microorganisms or enzymes in the soil.

Polyglycolide is known to be a biodegradable (including hydrolysable) high molecular compound. This compound has a high melting point and so is excellent in heat-resistance, but also it has high crystallinity and is brittle. Accordingly, this compound by itself has not yet been used practically as a plastics material.

EP-A-0446852, which is in the state of the art by virtue of Article 54(3) EPC, discloses compositions of a thermoplastic polymer, such as polyethylene or polypropylene or a polymer of caprolactone, containing up to 5% by weight of a polyglycolic acid as a nucleating agent. These compositions may be injection molded into a desired shape.

It is an object of the present invention to provide a biodegradable plastic composition practically useful as a material for shaped plastics articles.

In accordance with one aspect of the present invention, there is provided a biodegradable plastics composition comprising polyglycolide and a high molecular weight substance selected from poly(3-hydroxybutyric acid), a copolymer of 3-hydroxybutyric acid and 3-hydroxyvaleric acid, polycaprolactone, polyglutamic acid, polyolefin, polyvinyl alcohol, polyalkylene oxide, cellulose acetate and mixtures thereof, said polyglycolide being present in an amount of 10-60% based on the total weight of said polyglycolide and said high molecular weight substance.

In another aspect, the present invention provides a shaped article obtained by a method comprising the steps of providing the above biodegradable plastics composition, heating said composition to a temperature sufficient to melt said composition, and molding said melted composition into a desired shape.

The polyglycolide to be used in the present invention is a crystalline polymer obtained, for example, by heating glycolic acid, an ester thereof, sodium chloroacetate or glycolide (US-A-2585427 issued to M.L. Beck; Chujo, K. et al, Makromolekulare Chem., 100, 262 (1967); and Hirono, H. et al, Kogyo Kagaku Zasshi, 67, 604(1964)). Polyglycolide is advantageously prepared by reacting carbon monoxide with formaldehyde or paraformaldehyde in the presence of an acidic catalyst to form a polyglycolide (Masuda, T. et al, Japanese Patent (Tokkyo Kokoku) No. 56-34205). Very high molecular weight polyglycolide may be obtained by a method including the steps of adding water or a lower alcohol to ordinary polyglycolide to cause a depolymerization reaction to form glycolic acid or a lower alcohol ester thereof, and then heating to cause polymerization (US-A-2668162 issued to C.E. Lowe). Such a high molecular weight polyglycolide is suitably used for the purpose of the present invention because of its excellent moldability. In the present invention, however, a polyglycolide having a relatively low molecular weight obtained by reacting carbon monoxide and formaldehyde in the presence of an acidic catalyst can also be used as the starting material. Generally, polyglycolides produced by any known method in addition to those described above may be used for the purpose of the present invention. In general, a polyglycolide having a number average molecular weight higher than 500, preferably within the range from 800 to 200,000, can advantageously be used in the present invention.

The high molecular weight substance to be used in the present invention, alone or in admixture, as the other essential constituent of the composition, i.e. the poly (3-hydroxybutyric acid), copolymer of 3-hydroxybutyric acid and 3-hydroxyvaleric acid, polycaprolactone, polyglutamic acid, polyolefin, polyvinyl alcohol, polyalkylene oxide and cellulose acetate, are all commercially available. Accordingly, these commercially available high molecular weight substances can be used as such for the other constituent of the present invention.

The molecular weight of the high molecular weight substance varies with the kind of substance but is generally in the range of 2,000-5,000,000, preferably 10,000-1,000,000. More particularly, in case poly(3-hydroxybutyric acid) is used, a preferable molecular weight is within the range of 20,000-1,000,000, more preferably 300,000-900,000. In case of a copolymer of 3-hydroxybutyric acid and 3-hydroxyvaleric acid, the proportion of both components is preferably within the range of 1:0.05 to 1:0.3 and the molecular weight thereof is preferably within the range of 10,000-1,000,000, more preferably 300,000-900,000. In case of polycaprolactone, the molecular weight is preferably within the range of 20,000-100,000, more preferably 30,000-60,000. In the case of polyglutamic acid, the molecular weight is preferably within the range of 20,000-80,000, more preferably 30,000-70,000. Illustrative of polyolefins suitably utilizable in the present invention are homopolymers of lower olefins and copolymers of lower olefins themselves or with other monomers, such as polyethylene, polypropylene, polybutylene, ethylene/propylene copolymer and ethylene/vinyl acetate copolymer. The molecular weight of the polyolefin used is preferably within the range of 20,000-1,000,000, more preferably 30,000-200,000. In case of polyvinyl alcohol, the pref-

erable molecular weight is within the range of 15,000-100,000, more preferably 20,000-90,000. Illustrative of suitable polyalkylene oxides are polyethylene oxides, polypropylene oxides and the like lower polyalkylene oxides. The molecular weight of the polyalkylene oxide is preferably within the range of 2,000-5,000,000, more preferably 10,000-1,000,000. In case cellulose acetate is used in the present invention as the starting material, its molecular weight is preferably within the range of 10,000-200,000.

The molecular weights of polyglycolide and the high molecular weight substance are suitably selected according to the kind of the high molecular weight substance and the desired properties (biodegradability and moldability) of the composition. If the high molecular weight substance by itself shows poor moldability, the polyglycolide is desired to have a molecular weight of at least 20,000.

It is of interest that some other plastics substances such as polyvinyl chloride and polystyrene are extremely poor in blend performance with polyglycolide, and a biodegradable plastics shaped article cannot be obtained practically from a blend of these substances and polyglycolide.

The biodegradable plastics composition of this invention can easily be obtained by blending the polyglycolide with one or more of the high molecular weight substances under fusion. The resulting molten blend can then be processed by the aid of a conventional heat molding machine to manufacture molded articles of a desired shape. For example, a film of a desired thickness can be manufactured by hot calendering or extruding the blend, and a container of any desired shape can be manufactured by a conventional molding technique. Such articles may be of a foamed or non-foamed form. In case of manufacturing a foamed article, a proper amount of a foaming agent is incorporated into the plastics composition before molding. The plastics composition may further contain suitable amounts of an inorganic filler, a pigment, an anti-oxidant or the like conventional auxiliary substances provided that the inherent characteristic of the composition, e.g. biodegradability and mechanical property, are not seriously be damaged.

In the biodegradable plastics composition of this invention the proportion of the polyglycolide is specifically limited to 10-60 % by weight, preferably 10-50 % by weight based on the total amount of the polyglycolide and the high molecular weight substance. If the proportion of the polyglycolide is less than 10 % by weight, the biodegradability of the composition will become poor. On the other hand, if the proportion of the polyglycolide is greater than 60 % by weight, the composition will become so inferior in heat moldability that the mechanical properties of the resultant shaped article will be unsatisfactory.

The plastics compositions of this invention which contain the polyglycolide have good biodegradability as a whole. Further, the compositions have good moldability and are thus suitable as a biodegradable plastics molding material. Molded articles obtained from the plastics compositions of this invention are not brittle, as seen in polyglycolide by itself, and possess excellent flexibility and toughness.

Among the high molecular weight substances, polyvinyl alcohol, poly(3-hydroxybutyric acid), copolymers of 3-hydroxybutyric acid and 3-hydroxyvaleric acid, polycaprolactone, polyglutamic acid and cellulose acetate are themselves biodegradable. Thus, the biodegradable plastics compositions of this invention containing these high molecular weight substances can be used as an entirely biodegradable plastic molding material. Even when the biodegradable plastic composition contains a polyolefin, a very high molecular weight polyalkylene oxide, or the like high molecular weight substance which, per se, is not biodegradable, molded articles manufactured therefrom can significantly be reduced in their bulkiness and disintegrated into fractions when left in the soil.

This invention will now be illustrated in more detail by way of the following Examples and Comparative Examples.

Example 1:

In a carbon monoxide atmosphere, a stainless steel autoclave was charged with 10.0 g of trioxane, 30 ml of dichloromethane and 4 mmol of chlorosulfonic acid. The autoclave was then charged with carbon monoxide under pressure until the inner pressure became 55 kg/cm^2, and the mixture was reacted for 2 hours while stirring the mixture and elevating the temperature up to 180 °C. After completion of the reaction, unreacted carbon monoxide was discharged and the content of the autoclave was washed out with acetone whereby 8.6 g of an acetone-insoluble polymer (polyglycolide having a molecular weight of about 1200 or higher) and 4.3 g of an acetone-soluble polymer (polyglycolide having a molecular weight less than about 1000) were obtained.

The acetone-soluble polymer in an amount 0.2 g was melted and blended with 0.8 g of poly(3-hydroxybutyric acid) having a molecular weight of about 500,000 and the resultant molten blend was pressurized through an extruder under pressure of 50 kg/cm^2 for 5 minutes at 150 °C whereby the polymer blend could be processed to a film, which was found to have a satisfactory flexibility.

The thus obtained film (4 cm x 4 cm sample) was burried in the soil (depth: 5 cm) and left therein for 4 weeks at 23-30 °C. As a result, the film remaining in the soil was only about 6 % of the original area.

Example 2:

The acetone-insoluble polymer in an amount of 0.5 g obtained in Example 1 was melted and blended with a copolymer of 3-hydroxybutyric acid and 3-hydroxyva-

leric acid (molecular weight: ca. 15,000; the content of 3-hydroxyvaleric acid: 17 %) and the resultant molten blend was processed to a film under the same condition as described in Example 1 whereby the resultant film was also found to have a satisfactory flexibility and biodegradability.

Comparative Example 1:

A film-shaping operation was carried out under the same condition as described in Example 1 except that polyvinyl chloride was used in place of 0.8 g of the poly (3-hydroxybutyric acid) described in Example 1. However, the polymer blend was extremely brittle and thus could not be processed into a film.

Example 3:

An experiment was carried out in the same manner as described in Example 1 except that 0.8 g of polyglutamic acid (molecular weight : about 50,000) was used in place of 0.8 g of the poly(3-hydroxybutyric acid) whereby a flexible, biodegradable film could be obtained.

Comparative Example 2

An Experiment was carried out in the same manner as described in Example 2 except that 0.5 g of the acetone-insoluble polymer was blended with 0.5 g of polystyrene whereby a film could not be obtained.

Example 4:

An experiment was carried out in the same manner as described in Example 1 except that 0.5 g of the acetone-insoluble polymer and 0.5 g of poly(ε-caprolactone) having a molecular weight of about 40,000 were used, and the resultant molten blend was subjected to a film-shaping operation as described in Example 1 under pressure of 50 kg/cm^2 for 5 minutes at 160 °C whereby a flexible, biodegradable film was obtained.

Example 5:

A film-shaping operation was carried out in the same manner as described Example 1 except that 0.2 g of the acetone-insoluble polymer and 0.8 g of a high density polyethylene were used, whereby the polymer blend could be processed into a film, which was found to have a satisfactory flexibility.

Example 6:

A film-shaping operation was carried out in the same manner as described in Example 5 except that 0.5 g of the acetone-insoluble polymer and 0.5 g of the high density polyethylene were used whereby the polymer blend could be processed into a film, which was found to have a satisfactory flexibility.

This film was subjected to a heat treatment in water for 1 hour at 100 °C whereby the film was hydrolyzed to reduce its weight by about 20 % by weight.

Comparative Example 3:

A film-shaping operation was carried out in the same manner as described in Example 5 except that polyvinyl chloride was used in the same amount as described in Example 1 in place of the high density polyethylene. However, the polymer blend was extremely brittle and thus could not be processed into film.

Example 7:

A film-shaping operation was carried out in the same manner as described in Example 5 except that 0.8 g of polypropylene was used in place of 0.8 g of the high density polyethylene whereby a flexible film could be obtained.

Comparative Example 4:

A film-shaping operation was carried out in the same manner as described in Example 5 except that 0.5 g of acetone-insoluble polymer and 0.5 g of polystyrene were used whereby a film could not be obtained.

Example 8:

An experiment was carried out in the same manner as described in Example 5 except that 0.5 g of the acetone-insoluble polymer and 0.5 g of a polyethylene oxide (molecular weight: ca. 20,000) were used, and the resultant molten polymer blend was subjected to a film-forming operation in the same manner as described in Example 4 whereby a flexible, biodisintegrable film was obtained.

Example 9:

An experiment was carried out in the same manner as described in Example 5 except that 0.5 g of the acetone-insoluble polymer and 0.5 g of a polyvinyl alcohol (molecular weight: ca. 90,000) were used, and the resultant molten polymer blend was subjected to a film-shaping operation as described in Example 1 under pressure of 50 kg/cm^2 for 5 minutes at 130 °C whereby a flexible, biodegradable film was obtained.

Example 10:

An experiment was carried out in the same manner as described in Example 5 except that 0.5 g of the acetone-insoluble polymer and 0.5 g of cellulose acetate (polymerization degree: about 150) were used whereby

a flexible, biodegradable film was obtained as well.

Claims

1. A biodegradable plastics composition comprising polyglycolide and a high molecular weight substance selected from poly(3-hydroxybutyric acid), a copolymer of 3-hydroxybutyric acid and 3-hydroxyvaleric acid, polycaprolactone, polyglutamic acid, polyolefin, polyvinyl alcohol, polyalkylene oxide, cellulose acetate and mixtures thereof, said polyglycolide being present in an amount of 10-60% based on the total weight of said polyglycolide and said high molecular weight substance.

2. A composition as claimed in Claim 1, wherein said polyglycolide has a number average molecular weight of at least 500.

3. A composition as claimed in Claim 2, wherein said polyglycolide has a number average molecular weight of 800-200,000.

4. A composition as claimed in any preceding claim, wherein said polyglycolide is present in an amount of 10-50% based on the total weight of said polyglycolide and said high molecular weight substance.

5. A shaped article obtained by a method comprising the steps of providing a biodegradable plastics composition according to any preceding claim, heating said composition to a temperature sufficient to melt said composition, and molding said melted composition into a desired shape.

Patentansprüche

1. Biologisch abbaubare Kunststoffzusammensetzung, bestehend aus Polyglycolid und einer Substanz mit hoher Molekülmasse, die ausgewählt wird unter Poly(3-hydroxybuttersäure), einem Copolymer der 3-Hydroxybuttersäure und der 3-Hydroxyvaleriansäure, Polycaprolacton, Polyglutaminsäure, Polyolefin, Polyvinylalkohol, Polyalkylenoxid, Celluloseacetat und Gemischen daraus, wobei das Polyglycolid zu einem Anteil von 10 bis 60 %, bezogen auf die Gesamtmasse an Polyglycolid und der Substanz mit hoher Molekülmasse, enthalten ist.

2. Zusammensetzung nach Anspruch 1, worin das Polyglycolid ein Zahlenmittel der Molekülmasse von mindestens 500 aufweist.

3. Zusammensetzung nach Anspruch 2. worin das Polyglycolid ein Zahlenmittel der Molekülmasse von 800 bis 200 000 hat.

4. Zusammensetzung nach einem der vorstehenden Ansprüche, worin das Polyglycolid in einer Menge von 10 bis 50 Masse%, bezogen auf die Gesamtmasse an Polyglycolid und der Substanz mit hoher Molekülmasse, enthalten ist.

5. Formteil, das nach einem Verfahren gewonnen wird, das die Schritte Bereitstellen einer biologisch abbaubaren Kunststoffzusammensetzung gemäß einem der vorstehenden Ansprüche, Erhitzen der Zusammensetzung bis auf eine Temperatur, die zum Schmelzen der Zusammensetzung ausreicht, und Formpressen der geschmolzenen Zusammensetzung in eine gewünschte Form umfaßt.

Revendications

1. Composition plastique biodégradable comprenant un polyglycolide et une substance à masse moléculaire élevée choisie parmi le poly(acide 3-hydroxybutirique), un copolymère de l'acide 3-hydroxybutyrique et de l'acide 3-hydroxyvalérique, le polycaprolactone, l'acide polyglutamique, la polyoléfine, l'alcool polyvinylique, l'oxyde de polyalkylène, l'acétate de cellulose, et des mélanges de ces éléments, ledit polyglycolide étant présent à raison de 10-60% sur la base du poids total dudit polyglycolide et de ladite substance à masse moléculaire élevée.

2. Composition selon la Revendication 1, dans laquelle ledit polyglycolide a une masse moléculaire moyenne d'au moins 500.

3. Composition selon la Revendication 2, dans laquelle ledit polyglycolide a une masse moléculaire moyenne de 800-200 000.

4. Composition selon l'une quelconque des revendications précédentes, dans laquelle ledit polyglycolide est présent à raison de 10-50% sur la base du poids total dudit polyglycolide et de ladite substance à masse moléculaire élevée.

5. Article formé obtenu par une méthode comprenant les étapes de fourniture d'une composition plastique biodégradable selon l'une quelconque des revendications précédentes, chauffage de ladite composition à une température suffisante pour faire fondre ladite composition, et moulage de ladite composition fondue en une forme voulue.